
(12) UK Patent Application (19) GB (11) 2 095 224 A

(21) Application No 8110903
(22) Date of filing 7 Apr 1981
(30) Priority data
(31) 138045
(32) 7 Apr 1980
(33) United States of America
(US)

(43) Application published
29 Sep 1982
(51) INT CL³

C02F 1/52
(52) Domestic classification
C1C 223 324 400 40Y B
C3R 35D1 35D3 35D4
35M 35P2 38B3B 38B3C
38D1A3 38D6 38D7X
38D8B 38N1H SX
C3Y B186 F260

(56) Documents cited
None

(58) Field of search
C1C

(71) Applicant
Nalco Chemical Company,
2901 Butterfield Road,
Oak Brook,
Illinois 60521,
United States of America

(72) Inventors
Edward Ballweber,
Radharkrishnan
Selvarajan,
Manuel Slovinsky

(74) Agents
Reddie & Grose,
16 Theobalds Road,
London,
WC1X 8PL

(54) Water turbidity reduction

(57) A method of reducing turbidity in water comprises adding to the water a cationic co-polymer of

copolymerisable compounds comprising (1) 2,4-bis(p.aminobenzyl)-aniline (BABA) or aniline and (2) at least one of (a) epichlorohydrin, (b) ethylene dichloride and (c) formaldehyde.

GB 2 095 224 A

SPECIFICATION

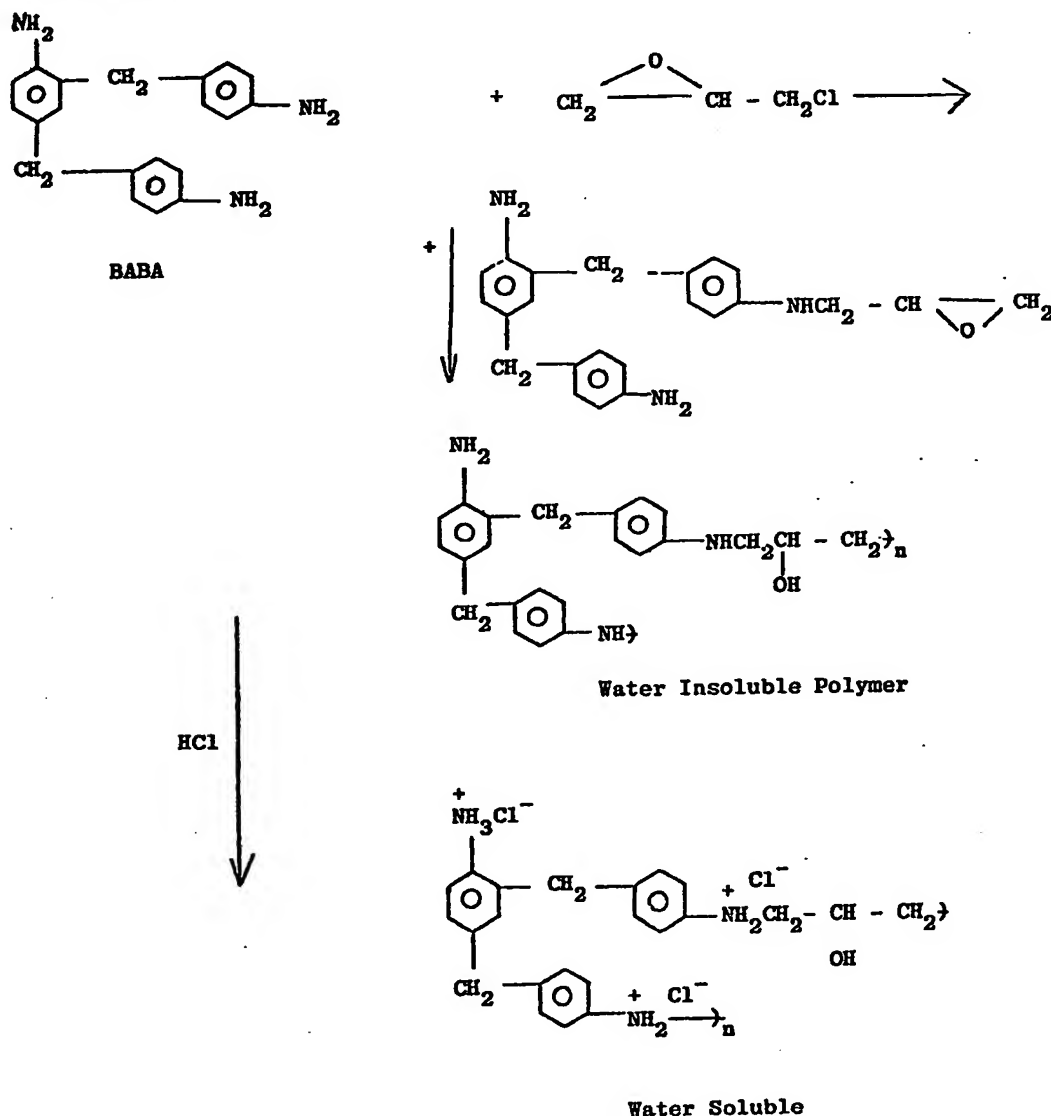
Water turbidity reduction

This invention relates to the reduction of water turbidity, especially such treatment of low turbidity water, and provides for the use, in reducing the turbidity of turbid water, of cationic copolymer of copolymerisable compounds comprising (1) 2,4-bis(p-aminobenzyl)aniline (BABA) or aniline (A) and (2) at least one of (a) epichlorohydrin (EPI), (b) ethylene dichloride (EDC) and (c) formaldehyde (F).

Low turbidity water generally has a 20—50 JTU (Jackson Turbidity Units) read-out; fully satisfactory clarification takes this down to a read-out of 2—5 JTU's.

The three highly branched cross-linked cationic polymers obtained by reacting 2,4-bis(p-aminobenzyl)aniline with (a) epichlorohydrin, (b) ethylenedichloride, and (c) formaldehyde are very active in the hydrochloride salt form in clarifying low-turbidity waters at low polymer dosage.

In a preparation of one such copolymer, for example, 2,4-bis(p-aminobenzyl)aniline is suspended in water at 95°C and reacted with epichlorohydrin and the product made homogeneous by rendering the solution highly acidic or to a pH of 0.5—1.0 with HCl. It is noted that an increase of pH to 3—4 leads to the precipitation of the polymer in colloidal form and this behaviour can be harnessed to clarify low turbidity waters. A schematic reaction path for this cationic copolymer is as follows:



One of the requirements for a polymer in actual use in reducing turbidity is that it forms fine flocculating particulates at about pH 7.0, which this polymer does.

In similar fashion the BABA monomer may be reacted with ethylene dichloride or formaldehyde to obtain effective polymers for clarifying low turbidity waters, e.g. to a clarity of 1 Jackson Turbidity Unit (JTU). These latter polymers have been given designation BABA-EDC and BABA-F.

Preferred copolymers for use according to the invention include the following: ethylene dichloride-ammonia polymer/aniline/formaldehyde (2:1.6:1.6); ethylene dichlorideammonia polymer/aniline/formaldehyde (1:2:2); ethylene dichloride-ammonia polymer/aniline/formaldehyde (2:1:1); DACH/aniline/formaldehyde (1:1:2); and DACH/aniline/formaldehyde (2.5:1:2.5). DACH is 1,2-diaminocyclohexane. An additional preferred polymer is aniline/tetraethylene pentamine (TEPA)/formaldehyde, where BABA may be substituted for aniline. The indicated ratios are molar ratios of the reactants.

An average replacement ratio (r/r_0 , defined below) of 0.3—0.9 against standard floc polymer has been noted for the above copolymers used according to the invention. Additionally, these amine formaldehyde polymers performed well, yielding good floc formation.

The above polymers yielded good floc formation and excellent water clarity and all operated to lower turbidity at a weight limit of 2.50 mg/kg (preferred 2.20 mg/kg) dosage range. The preferred ratio of monomers in the two-component polymer is 3:1 to 1:3 except where contra indicated herein. For ternary polymers a preferred ratio is 1:2:1.

Additional data regarding BABA polymers is submitted in the following Table 1.

Table 1
Condensation Polymers of BABA*

Name	Correctant Moles	HCl Moles	Ratio of BABA: Co-Reactant:HCl	Reaction T°C	Prod. Conc. %	Cationic Charge at pH 4.0 Meq	PPM Actives for <5 JTU	Raw Material Cost \$/lb.	Remarks
Epi Formaldehyde	0.097	0.245	1:1:2.5	95	1.0	26.7	6.0	0.949	
Formaldehyde	0.05	0.3	1:0.5:3	95	2.0	10.4	9.0		Reaction pH 2.5
Formaldehyde	0.075	0.3	1:0.75:3	95	5	14.99	9.0		Reaction pH 0.2
Formaldehyde	0.1	0.3	1:1:3	75	2	24.42	7.5	0.0799	Reaction pH 0.1
EDC	0.2	0.4	1:1:2	98	2	25.1	9.0	0.0792	Product pH 1.2

*2,4-Bis(p-aminobenzyl)aniline, m.p. 72—76°C, a reactant throughout

Aniline-F polymers

In a consideration of how structure contributes to activity, aniline was also utilized in the present invention in condensations with formaldehyde. In comparison with BABA, a substituted aniline, it is obvious that BABA can be obtained as one of the products from aniline-formaldehyde (aniline-F) condensation. Additionally, aniline being a liquid offers advantages over BABA in handling.

In the polymerization process, aniline was suspended in water and treated with an equimolar quantity of hydrochloric acid. The clear solution, pH 0.1, was heated to 100°C and then reacted with formaldehyde for 3 hrs. In the experimental data, the mole ratio of F/aniline ranged from 1—2. Mole ratios in excess of 1.5 led to a highly crosslinked insoluble gel and therefore a mole ratio of F/aniline below 1.5 is to be utilized where aniline is used as a component. For replacement tests, in a 20 ppm Kaolin jar test, a replacement ratio of 0.756 was observed when compared to other flocculant (Magnifloc).

The formation of aniline-F resin, polymethylene aniline, can be depicted in terms of the following over-simplified reaction scheme:

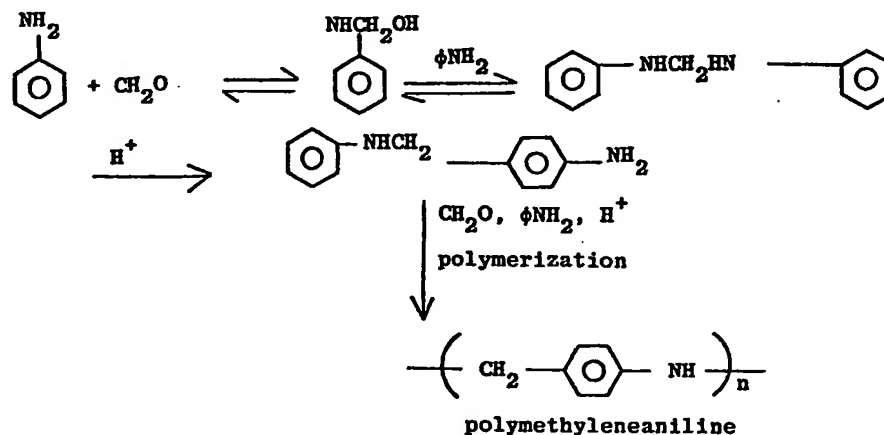


Table 2 shows the synthesis and activity of copolymers of formaldehyde-arylamines and Table 3 shows the synthesis and activity of terpolymers of aniline, formaldehyde, and amines.

Table 2
Synthesis and Activity of Copolymers of Formaldehyde-arylamines

Polymer Characteristics				Water Clarification				
Type	Mole Ratio	% Solids	pH	Water Source and/or Type	ppm Actives Dose	Lowest JTU	r/r _o Actives Basis	
A—F	1:2	18.49	<0.1	20 ppm Kaolin		2	—	
A—F	1:1	19.88	<0.1				1.0	
A—F	1:1	19.88	<0.1				1.3	
A—F	1:1	10.0	<0.1	20 ppm Kaolin	Copolymer	2	1.1	
A—F	1:1	19.97	<0.9	20 ppm Kaolin			0.73	
A—F	1:1	30.0	<0.1	Copolymer			0.2	
A—F	1:1	38.0	<0.1	Copolymer			0.4	
A—F	1:1	40.0	<0.1				—	
A—F	1:1.25	25.0	<0.1	Copolymer	Copolymer		0.2	
A—F	1:1.25	25.0	<0.1	Copolymer			0.33	
A—F	1:1.25	30.0	<0.1	Copolymer				
A—F	1:1.5	11.72	<0.1	20 ppm Kaolin	Copolymer	2	0.26	
A—F	1:1.5	13.63	<0.1	20 ppm Kaolin			0.26	
A—F	1:1.5	15.0	<0.1	Copolymer			0.17	
A—F	1:1.5	10.0	<0.1	Copolymer			0.17	
ØNMe ₃ Cl—F	1:1	30.0	—					
2,4-Toluenediamine-F	1:1.25	15.0	<0.1	Copolymer	2.5	2.5	1.1	
2,4-Toluenediamine-F	1:2	10.1	<0.1	Copolymer	2.5	2.0		
2,3-Toluenediamine-F	1:1.25	20.0	<0.1	—		7.0	—	
Diphenylamine-F						—	—	
m-Aminophenol-F							—	
o-Aminophenol-F	1:1.22	20.0	<0.1	Copolymer	poor v. poor			
N,N-DMA-F	1:1.25	25.2	<0.1					
N,N-DMA-F	1:1	20.0	<0.1					
N,N-DMA-F	1:1	40.0	<0.1					

A=aniline
F=formaldehyde
N,N-DMA-F=N,N-dimethylaniline-formaldehyde

Table 3
Synthesis and Activity of Terpolymers of Aniline, Formaldehyde and Amines

Polymer Composition			Reaction Conditions				Water Clarification	
Type	Mole Ratio	Reaction Mode	T°C	t _{hrs}	pH	% Solids	Water Type and/or Source	r/r _o Actives Basis
A—DACH F	1:1:2	A+DACH+HCl+F	95	0.5	0.5	10.0	20 ppm Kaolin	—
A—DACH F	1:1:2	A+DACH+HCl+F	95	0.5	0.5	10.0		—
A—DACH F	1:1:2.5	A+DACH+HCl+F	98	4.0	0.5	23.0		poor
A—DACH F	1:1:3	A+DACH+HCl+F	95	1.0	0.5	25.0		—
A—DACH F	1:1:3	A+DACH+HCl+F	95	1.0	0.5	10.56		—
A—DACH F	1:1:3	A+DACH+HCl+F	85	0.25	0.5	10.0		—
A—DACH F	1:1.33:3	A+DACH+HCl+F	95	0.5	0.5	17.73		—
A—DACH F	1:1.33:3.6	A+DACH+HCl+F	85	0.25	0.5	10.0		—

Table 3 (continued)
 Synthesis and Activity of Terpolymers of Aniline,
 Formaldehyde and Amines

Polymer Composition		Reaction Conditions					Water Clarification	
Type	Mole Ratio	Reaction Mode	T°C	t _{hrs}	pH	% Solids	Water Type and/or Source	r/r _o Actives Basis
A-DACH F	1:1.5:3		85	1.0	0.5	17.75		—
A-DACH F	1.2:1:2.5	AF+DACHF+HCl	95	5.0	0.5	17.91		—
A-DACH F	1.25:1:2.6	A+DACH+HCl+F	95	1.0	0.5	20.0		—
A-DACH F	2:1:3	A+DACH+HCl+F	98	2.5	0.5	5.0		—
A-DACH F	3:1:4	A+DACH+HCl+F	98	4.5	0.5	10.0	20 ppm Kaolin	1.0
A-DACH F	4:1:5	A+DACH+HCl+F	98	3.0	0.5	20.0	20 ppm Kaolin	6.0
A-DACH F	4:1:5	A+DACH+HCl+F	95	4.5	0.5	10.0	20 ppm Kaolin	1.0
A-DACH F	1:2:5	A+DACH+HCl+F	95	0.5	0.5	10.0		—
A-DACH F	1:1:1.27	A+DACH+HCl+F	98	3.5	0.2	12.0	20 ppm Kaolin	1.4
A-DACH F	1:1:2	A+DACH+HCl+F	98	2.0	0.2	25.4		—
A-DACH F	1:1:2	DACH . F . HCl+A	98	2.0	0.2	25.4		—
A-DACH F	1:1:2	A+DACH+HCl+F	98	1.0	0.2	15.0		—
A-DACH F	1:1:2	A . DACH . F+HCl	98	1.0	0.2	20.15		—
A-DACH F	1:1:2	DACH . F . HCl+A	98	4.0	0.2	20.0		—
A-DACH F	1:1:2.28	DACH . F . HCl+A	98	3.0	0.2	16.89		—
A-DACH F	1:1:2.5	A . DACH . F+HCl	100	3.0	0.2	25.0		—
A-DACH F	1:1:2.5	A+DACH+HCl+F	100	0.5	0.2	25.0		—
A-DACH F	1:1:19:2	DACH . F . HCl+A	100	3.5	0.4	19.65	20 ppm Kaolin	1.7
A-DACH F	1:1:19:2.25	DACH . F . HCl+A	100	4.5	0.4	19.57	20 ppm Kaolin	1.3
A-DACH F	1:1:19:2.5	DACH . F . HCl+A+F	100	4.0	0.4	10.0		—
A-DACH F	1:1:25:2.38	DACH . F . HCl+AF . HCl	80	0.5	0.1	25.0		—
A-DACH F	1:1:25:2.38	DACH . F . HCl+AF . HCl	80	0.5	0.1	16.66		—
A-DACH F	1:1:3:2.3	DACH . F . HCl+A	96	2.5	0.1	15.0		—
A-DACH F	1:1:3:2.6	DACH . F . HCl+A	96	2.5	0.1	15.0		—
A-DACH F	1:2:2	A+DACH+HCl+F	96	1.0	0.1	20.0		—
A-DACH F	1:2:2	DACH . F . HCl+A	96	3.0	0.1	19.8	20 ppm Kaolin	1.9
A:DACH:F	1:2:2	A . DACH . F+HCl	100	3.0	0.1	10.0		—
A:DACH:F	1:2:2.5	DACH . F . HCl+A	98	6.0	0.2	10.0	20 ppm Kaolin	2.8
A:DACH:F	1:2:3	AHCl . F+DACH	102	3.0	0.2	25.0	20 ppm Kaolin	poor
A:DACH:F	1:2:3	AHCl . F+DACH	102	4.0	0.2	20.0		—
A:DACH:F	1:2:3	A . DACH . HCl+F	100	0.25	0.2	20.0		—
A:DACH:F	1:2:3	DACH . HCl . F+A	96	2.5	0.2	14.84		—
A:DACH:F	1:2:3	DACH . HCl . F+A	96	3.5	0.2	10.0		—
A:DACH:F	1:2:4	A . HCl . F+DACH	102	6.0	0.2	24.53	20 ppm Kaolin	poor
A:DACH:F	1:2.5:2.5	DACH . HCl . F+A	98	2.5	0.2	20.0	20 ppm Kaolin	1
A:DACH:F	1:2.5:2.5	DACH . HCl . F+A	98	3.0	0.2	30.0	20 ppm Kaolin	1
A:DACH:F	1:2.5:2.5	DACH . HCl . F+A	98	3.0	0.2	35.43	20 ppm Kaolin	2.0
A:DACH:F	1:2.5:3	DACH . HCl . F+A	98	4.5	0.2	15.2	20 ppm Kaolin	1
A:DACH:F	1:3:3	DACH . HCl . F+A	98	2.5	0.2	20.8	20 ppm Kaolin	poor
A:DACH:F	1:3:4	DACH . HCl . F+A	98	4.5	0.2	15.96	20 ppm Kaolin	poor
A:DACH:F	1:3:4	A . HCl+F+DACH	102	6.0	0.2	25.0	20 ppm Kaolin	poor
A:DACH:F	1:3:4	A . HCl+F+DACH	102	6.0	0.2	24.65	20 ppm Kaolin	poor
A:DACH:F	1.5:1:1.66	A . DACH . HCl+F	98	3.0	0.5	18.85	20 ppm Kaolin	1.1
A:DACH:F	1.5:1:2	A . DACH . HCl+F	98	3.5	0.5	18.63		—
A:DACH:F	1.5:1:2	A . DACH . HCl+F	98	5.0	0.5	12.0	20 ppm Kaolin	1.1
A:DACH:F	2:1:2	A . DACH . HCl+F	98	2.5	0.5	20.0	20 ppm Kaolin	1.5
A:DACH:F	2:1:2.5	A . DACH . HCl+F	98	2.5	0.5	15.0	20 ppm Kaolin	1.0
A:DACH:F	2:1:3	A . DACH . HCl+F	98	5.0	0.5	20.0		—
A-HMDA-F	1:0.5:1.5	A . HMDA . HCl+F	35	—	0.5	16.9		—
A-HMDA-F	1:1:1	AF . HCl+HMDA . HCl	40	—	0.5	20.0		—
A-HMDA-F	1:1:2	A . HMDA . F . HCl+F	100	1.0	0.5	16.3		—
A-HMDA-F	1:1:2.5	A+HMDA+HCl+F	100	0.5	0.5	22.5		—

Table 3 (continued)
*Synthesis and Activity of Terpolymers of Aniline,
 Formaldehyde and Amines*

Polymer Composition		Reaction Conditions					Water Clarification	
Type	Mole Ratio	Reaction Mode	T°C	t _{hrs}	pH	% Solids	Water Type and/or Source	r/r ₀ Actives Basis
A-HMDA-F	2:1:2	HMDA . F . HCl+A	100	2.5	0	18.76		—
A-HMDA-F	2:1:2	HMDA . F . HCl+A	100	3.0	0	21.2	20 ppm Kaolin	1.2
A-HMDA-F	2:1:2.4	HMDA . F . HCl+A	100	6.0	0	17.34	20 ppm Kaolin	1.0
A-HMDA-F	2:1:2.4	HMDA . F . HCl+A+F	100	5.0	0	18.0	20 ppm Kaolin	—
A-HMDA-F	2:1:2.4	HMDA . F . HCl+A+F	100	5.0	0	18.0	20 ppm Kaolin	—
						12.0	20 ppm Kaolin	1.3
A-HMDA-F	2:1:3	A+HMDA+HCl+F	100	4.0	0	10.0	20 ppm Kaolin	—
A-HMI-F	1:2:2	A+HMI+HCl+F	100	3.0	0	25.0	20 ppm Kaolin	1.0
A-HMI-F	1:2:2.5	A+HMI+HCl+F	100	5.5	0	24.71	20 ppm Kaolin	0.9
A-HMI-F	1:4:4	A+HMI+HCl+F	100	3.0	0	25.0	20 ppm Kaolin	0.9
A-HMI-F	1:4:5	A+HMI+HCl+F	100	5.0	0	24.8	20 ppm Kaolin	0.7
A-ED-F	1:1:2	E . F . HCl+A	100	2.0	0	20.0	20 ppm Kaolin	1.0
A-ED-F	1:1:2.5	ED . F . HCl+A	100	4.0	0	19.78	20 ppm Kaolin	0.8
A-TEPA-F	5:1:10	TEPA . F . HCl+A	95	3.0	0	20.0	20 ppm Kaolin	1.0
A-TEPA-F	5:1:12.5	TEPA . F . HCl+A	95	4.0	0	19.75	20 ppm Kaolin	0.6
A-DEA-F	2:1:2.5	A+DEA+HCl+F	95	3.0	0	15.0	20 ppm Kaolin	1.0
A-M-F	6:1:8	MF+A+HCl	95	5.0	0	12.59	20 ppm Kaolin	1.0
A-M-F	1:1:2	MF+A+HCl	60	5.0	0	9.6		—
A-M-F	1:2:2	MF+A+HCl			0	6.5		—
A-Ar . C-F	4:1:5.5	A+Ar . C+HCl+F	100	2.5	0	10.0	20 ppm Kaolin	0.75
A-Ar . T-F	8:1:9.5	A+Ar . T+HCl+F	100	4.0	0	13.68	20 ppm Kaolin	1.0
A-Duo . C-F	8:1:9.5	A+Duo . C+HCl+F	100	2.0	0	15.0		1.2
A-N,N . DMA-F	1:1:2.5	A+N,N-DMA+HCl+F	96	6.0	0	25.0	20 ppm Kaolin	0.56
A-N,N . DMA-F	1:2:3.75	A+N,N-DMA+HCl+F	96	6.0	0	25.0	20 ppm Kaolin	1.2

Additional additive components

- In an aniline-formaldehyde (A—F), modification has been made with (i) phenol such as tertiary butyl phenol and nonyl phenol, (ii) diamines such as diamino cyclohexane (DACH),
 35 hexamethylenediamine (HMDA), (iii) secondary amines such as diethanolamine (DEA) and hexamethylenimine (HMI), and (ii) polyamines and fatty (C₁₂—C₁₈) amines such as cocoamine, cocodiamine, and tallow amine.

- Additionally, the formaldehyde component of the preferred polymer was substituted unsuccessfully with furfural, glyoxal, and butyraldehyde. In these cases the substitution in the basic
 40 polymer led to gelation or charring.

Example 1A

BABA—Epi

- Powdered BABA was suspended in water and the mixture was heated with stirring. As the temperature reached around 75°C the amine melted and an easily stirrable heterogeneous mixture
 45 resulted. As the temperature reached 95°C Epi was added and the reaction was continued for 1 hr at 95°C. Assuming that the amine was 100% pure, the mole ratio of BABA to Epi was held at 1:1. After an hour of reaction, no homogeneity nor solid separation was noticed. However, upon adding hydrochloric acid, a dark homogeneous solution, pH 2.0, was obtained. But upon three-fourfold dilution of the product, precipitation was noticed. More HCl was added to the product and rendered it highly
 50 acidic, pH 0.5, whereupon the product sustained infinite dilution; i.e., no turbidity was noticeable to the naked eye. The product at 6 ppm actives would clarify Des Plaines river water to a turbidity below 5 JTU.

1:1 Polymer

Reaction Ingredients	g	Moles	%
BABA	31.0	0.102	22.5
DI water	73.0		53.18
Epi	9.0	0.097	6.5
Hydrochloric Acid (36%)	24.5		17.82
	137.5		100.0

Polymerization steps

1) A resin flask fitted with a pressure equalizer was charged with powdered BABA and water.

2) The mixture was heated and the stirring was turned on as soon as the reaction mixture attained 80°C.

3) Epi was added to the hot solution over 5 minutes with continued heating.

4) In about 0.5 hr only water was seen refluxing at 102°C and an unstable emulsion of the polyamine in water has noticed.

5) Upon adding the hydrochloric acid, a dark brown clear solution was obtained readily.

6) While computing the polymer solids, the elimination of stoichiometric amount of HCl, based on Epi, was recognized.

Products characteristics

Polymer solids = 26.5%

I.V., dl/g = 0.0448

pH = 0.1

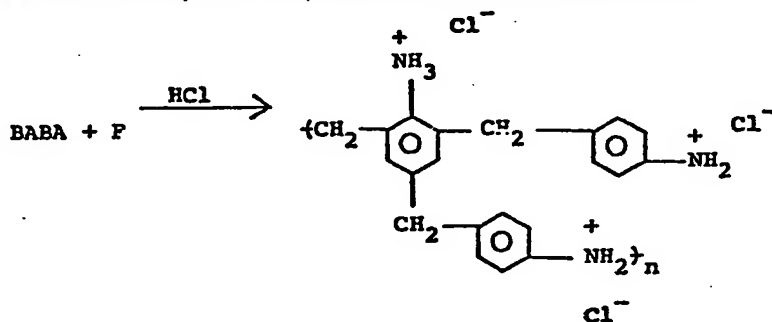
Cationic charge at pH 4.0 = 6 meq/mg

Example 1B

BABA-Formaldehyde

The amine was reacted with formaldehyde. Since the reaction of the amine and F was instantaneous at the inherent basic pH, the product precipitated and stirring problems were encountered. As a result, further experiments were conducted in highly acidic homogeneous amine hydrochloride solutions with varying BABA/F mole ratios. The product, wherein the mole ratio of BABA:F:HCl is 1:1:3, has shown remarkable activity; i.e., 2 ppm actives reduced the river water turbidity below 5 JTU. Even though the activity is almost comparable to that of Magnifloc 515C (melamine-formaldehyde polymer, American Cyanamide), from the past experience, an absolute conclusion could not be drawn without testing both samples under identical conditions.

For convenience the product may be structurally represented as below:



The above structure is assigned cognizant of the fact that the methylene bridges between the benzene rings are formed ultimately in aniline type compounds in presence of formaldehyde and in strongly acid solution.

1:1 Polymer

1:2 Polymers

Reaction Ingredients	g	Moles	%	g	Moles	%
BABA	30	0.0993	23.43	30	0.099	22.9
HCl, 36%	30		23.43	30		22.9
D.I. Water	60		46.88	55		41.89
F, 37%	8	0.099	6.25	16	0.197	12.21
	128		100.00	131		100.00

Polymerization steps

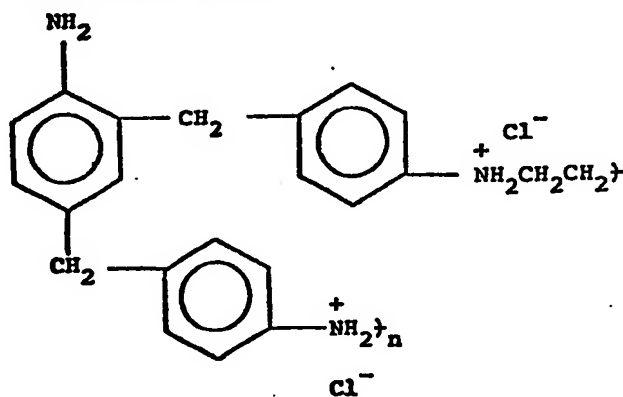
- 1) A resin flask fitted with a pressure equalizer was charged with powdered BABA and water.
- 2) The mixture was heated and stirring was started after the reaction mixture attained 80°C.
- 3) Hydrochloric acid was added rapidly and a clear brown solution resulted.
- 4) As the solution was being heated, 90°C, the formaldehyde solution was added over a 5 minutes period.
- 5) The solution was kept refluxing, 95—98°C, for 3 hours and the nonviscous product collected.
- 6) Based on formaldehyde, the elimination of stoichiometric amounts of water was reckoned while calculating the polymer solids.

Product characteristics

	1:1 Polymer	1:2 Polymer
Polymers solids =	24.42%	24.7%
Cationic charge at pH 4.0/mg =	7.5 meq.	5.8 meq.
pH =	0.1	0.1

**Example 1C
BABA—EDC**

EDC was reacted with BABA in an autoclave. The amine and EDC were reacted at 1:1 mole ratio, at 98°C/2 hrs, and the product was rendered homogeneous by adding HCl. At 7 ppm actives, the product clarified the river water to the desired level. The product may be structurally represented as below with branching or crosslinking interspersed.

**1:1 Polymer**

	Reaction Ingredients	g	Moles	%
	BABA	60.0	0.198	23.1
	DI water	140.0		53.9
	EDC	19.6	0.198	7.6
	Hydrochloric acid (36%)	40.0		15.4
		259.6		100.0

Polymerization steps

- 1) Crushed BABA and water were charged into a 1 liter autoclave and the autoclave was heated without turning the stirrer on.
- 2) When the reaction mixture attained 80°C (Mp. of BABA=72—76°C, 170°F) the stirring was turned on.
- 3) EDC was pumped in slowly over 15 minutes. When the reaction mixture attained 100°C, a mild exotherm was noticed but no detectable increase in pressure was registered.
- 4) The mixture was kept heated for 2 hours at 100°C.
- 5) It was then cooled to 80°C and the hydrochloric acid was pumped in.
- 6) While computing the polymer solids, the elimination of twice the molar quantities of HCl based on EDC was reckoned.

Product characteristics

Polymers solids = 25.1%
I.V., dl/g = 0.0412
Cationic charge at pH 4.0/mg = 9.0 meq.
pH = 0.1

Example 2**Antiline-F, 1:1 and 1:1.5, polymers**

<i>Reaction Ingredients</i>	<i>1:1 Polymer</i>			<i>1:1.5 Polymer</i>			
	<i>g</i>	<i>Moles</i>	<i>%</i>	<i>g</i>	<i>Moles</i>	<i>%</i>	
5 Aniline	74.4	0.8	17.61	74.4	0.8	11.42	5
DI water	200.0		47.35	396.6		60.87	
HCl, 36%	83.2	0.82	19.7	83.2	0.82	12.77	
F, 37%	64.8	0.8	15.34	97.3	1.2	14.93	
	422.4		100.0	651.5		100.0	

10 Polymerization steps

1) A resin flask fitted with a pressure equalizer was charged with aniline and water.
 2) To the stirred mixture hydrochloric acid was added over a 0.5 hour period. The temperature rose to 50°C owing to the heat of neutralization.

3) The solution was heated and the formaldehyde solution was added when the temperature reached about 80°C.

4) The intense orange solution was kept refluxed, 95—98°C, for 3 hours and the nonviscous polymeric product collected.

5) Based on formaldehyde, the elimination of stoichiometric amounts of water was reckoned while calculating the polymer solids.

20 Product characteristics

	<i>1:1 Polymer</i>	<i>1:1.5 Polymer</i>
Polymer solids =	19.97%	13.63%
Cationic charge at 4.0/mg =	7.5 meq.	4.9 meq.
pH =	0.1	0.1

25 Example 3**EDC-Ammonia polymer/aniline/formaldehyde**

<i>Reactants</i>	<i>g</i>	<i>Moles</i>	<i>Wt. %</i>	
EDC-ammonia, 39% polymer	21.6	0.2	8.5	
Aniline	37.2	0.4	14.7	
Water	101.2		40.0	30
Hydrochloric acid (36%)	60.6	0.6	23.9	
Formaldehyde (37%)	32.4	0.4	12.8	
	253.0		99.9	

Polymerization steps

1) A 500 ml resin flask fitted with a stirrer, condenser and addition funnel was charged with EDC-ammonia (39% polymer), aniline and water.

2) Hydrochloric acid was added with stirring. A mild exotherm raised the temperature to 35°C.

3) Formaldehyde was then added dropwise over 10 mins. Fine yellow particles were seen suspended.

4) Upon heating the mixture to reflux temperature, 100°C, a clear reddish-brown solution was obtained. The refluxing was continued for 2 hours.

5) The dark brown solution was cooled and collected.

Product characteristics

Polymer solids = 20%

pH = 0.1

Color = Dark brown

Example 4**Aniline/1,2-diaminocyclohexane/formaldehyde**

	<i>Reactants</i>	<i>g</i>	<i>Moles</i>	<i>Wt. %</i>	
5	1,2-diaminocyclohexane (DuPont)	58.0	0.5	14.04	5
	Water	179.9		43.58	
	Hydrochloric acid (36%)	116.0	1.14	28.08	
	Formaldehyde (37%)	40.5	0.5	9.8	
	Aniline	18.6	0.2	4.5	
		413.0		100.0	

10 Polymerization steps

1) A one-liter resin flask fitted with stirrer, condenser and addition funnel was charged with diaminocyclohexane and water.

2) Hydrochloric acid, 101 g was added to the amine with stirring. The exotherm raised the temperature from 25°C to 55°C. Copious white fuming was also noticed. The solution pH was 0.7.

15 3) To the hot amine hydrochloride formaldehyde was added over 5 minutes. A mild exotherm due to the methylation raised the temperature to 60°C.

4) The solution was then heated to 70°C and held for one hour.

20 5) To the hot brown solution, the rest of the hydrochloric acid, 15 g, was added followed by the dropwise, 15 minutes, addition of aniline. The precipitation and rapid dissolution of a yellow solid was noticed.

6) The reaction mixture was then heated to reflux, 98°C, and held for 3 hours.

7) Upon cooling, the product (a clear brown solution) was obtained.

Product characteristics

25 Polymer solids = 20%
pH = 0.1
Color = Dark brown

Example 5**Aniline/hexamethylenediamine/formaldehyde**

30 A condensation terpolymer of aniline, hexamethylenediamine and formaldehyde showed excellent activity in the clarification of activated sludge.

	<i>Reactants</i>	<i>g</i>	<i>Moles</i>	<i>Wt. %</i>	
35	Aniline	10.93	0.1175	10.11	35
	Hexamethylenediamine (70%)	9.76	0.0589	9.03	
	Water	52.97		49.0	
	Hydrochloric Acid (36%)	22.92	0.226	21.2	
	Formaldehyde (37%)	11.52	0.142	10.66	
		108.1		100.00	

Polymerization steps

40 1) A 500 ml resin flask fitted with stirrer, condenser, and addition funnel was charged with hydrochloric acid, 12 g, and water, 35.15 g.

2) Hexamethylenediamine was then added with stirring. An exotherm accompanied the evolution of dense white fumes.

3) To the warm amine salt solution, 50°C, formaldehyde, 9.52 g, was added rapidly and the mixture was kept stirred for 30 minutes at 70°C.

45 4) The rest of the HCl, 10.92 g, was added, followed by the rapid addition of aniline.

5) The solution was heated to 100°C and a clear red solution was seen refluxing.

6) After refluxing the mixture for 3 hours, water, 17.82 g, and formaldehyde, 2 g, were added. The reaction was continued further for 2 hours, and after cooling, the product (a clear brown watery solution) was collected.

50 Product characteristics

Polymer solids = 18.00%
Color = Dark brown
pH = 0.1

Example 6**Branched/cross-linked polyamines from BABA**

BABA, a dark brown solid, mp 75—76°C, readily formed a water-soluble hydrochloride. The salt facilitated the one-step synthesis of BABA-F polymers. A number of experiments (see Table 4) with mole ratios F/BABA ranging from 0.5—3.0 were tried. A molecule of BABA has three amino groups and five ortho positions to participate in the methylene bridging,

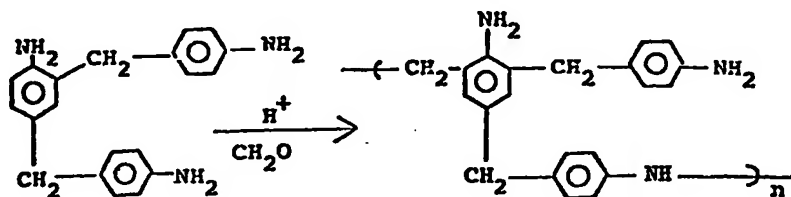
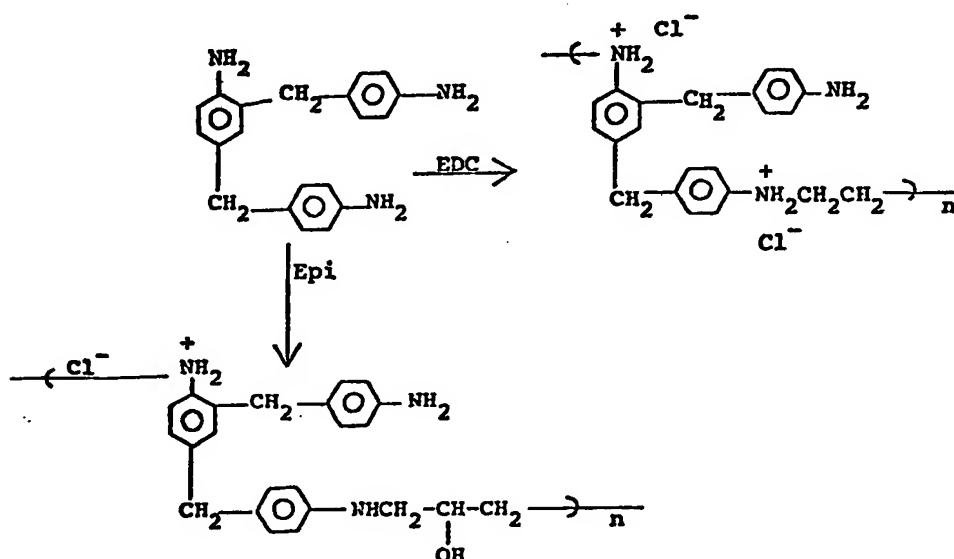


Table 4
Synthesis and Activity of Polyamines from BABA
Polymer Characteristics *Water Clarification*

	Type	Mole Ratio	% Solids	pH	Water Clarification	
					Water Source and/or Type	r/r _o Actives Basis
15	BABA-F	1:0.5	10.4	0.3		
	BABA-F	1:0.75	14.99	0.2	D. P. River	0.67
	BABA-F	1:1	24.42	0.1	D. P. River	0.67
	BABA-F	1:2	24.7	0.2	D. P. River	0.53
	BABA-F	1:2	30.5	0.2	D. P. River	0.8
20	BABA-F	1:3	15.0	0.2		—
	BABA-F	1:3	8.2	0.2	D. P. River	1.0
	BABA-F	1:2	23.79	0.2	20 ppm Kaolin	1.0
	BABA-F	1:1	24.4	0.1	20 ppm Kaolin	0.94
	BABA-F	1:1	24.4	0.1	20 ppm Kaolin	0.94
25	BABA-Epi	1:1	26.7	—	D. P. River	1.2
	BABA-Epi	1:2	29.0	—		
	BABA-Epi	1:2	10.0	—		
	BABA-Epi	1:2	100.0	—	D. P. River	0.67
	BABA-Epi	1:1	39.9	—	—	—
30	BABA-Epi	1:1.5	40.0	—	—	—
	BABA-Epi	1:1.5	20.0	—	—	—
	BABA-Epi	1:1.5	20.0	—	—	—
35	BABA-EDC	1:1	25.1	—	copolymer	0.9
	BABA-EDC	1:1.5	30.7	—		—
	BABA-EDC	1:1.25	30.8	—		—

The presence of a number of reactive amino groups in a molecule of BABA stimulated interest in reacting it with Epichlorohydrin (Epi) and Ethylenedichloride (EDC) independently. The reactions were carried out at the inherent pH of the medium.

Incorporation of EDC or Epi in excess of molar equivalents of BABA led to gelation



The polymers arising out of the reaction of molar equivalents of BABA-Epi and BABA-EDC were not soluble until an acid sufficient to protonate all the amine groups was added. For convenience, the polymerization sequence is represented as above.

5 Example 7

In the reaction below for the production of a terpolymer of aniline-tetraethylene pentamine (TEPA)formaldehyde, 31.5% concentrated HCl was used in the run.

Reactants	g	Moles	Wt. %
Aniline	46.5	0.5	12.03
TEPA	20.8	0.11	5.38
Hydrochloric acid 20 Baume, 31.45%	123.0	1.06	31.84
Formaldehyde, 37%	81.0	1.0	20.96
D.I. Water	115.0		29.76
	386.3		99.97

As polymerization steps, the following regimen was followed:

1. A 500 ml resin flask fitted with a stirrer, condenser and addition funnel was charged with hydrochloric acid, 123 g and deionized water, 115 g.

2. TEPA, 20.8 g, was then added with stirring over 5 minutes. Dense white fumes and exotherm were noticed. The reaction temperature was 60°C.

3. To the hot amine salt solution, formaldehyde, 81 g, was added over 10 minutes. The dark brown solution was kept heated at 80°C for 0.5 hour.

4. Then aniline, 46.5 g, was added in rapidly. The dark brown solution, pH 0.3, was kept refluxed (95—96°C) for 3 hours and the clear nonviscous polymer product collected, 20.52% actives.

Product characteristics

Polymer solids = 20.52%

Color = Dark brown

pH = 0.3

In the above Examples and Tables, "DI water" means de-ionized water, and "D.P. river" means the Des Plaines river; r/r_0 defines replacement ratio, a dimensionless number—lower values indicate a higher activity of a given material on a weight or active basis over a given standard material and higher values than 1.0 conversely indicate poorer activity on a weight basis than the standard material compared; in all of these tests, the materials of this invention were compared against a commercial flocculating polymer derived from melamine formaldehyde reactions. "Copolymer" in Table 2 refers to industrial waste water which contains suspended carbon and an SBR copolymer latex waste, the water having turbidity of 20—30 JTU's.

Some of the cationic copolymers disclosed herein (particularly those of BABA), and the aqueous solutions thereof, are novel per se, and form part of this invention.

The invention provides for treating low turbidity waters with cationic co-polymers and

terpolymers which have a component of aniline or 2,4-bis(p-aminobenzyl)aniline (BABA) reacted with at least one of a group consisting of epichlorohydrin, ethylene dichloride, and formaldehyde. Additionally, terpolymers may include aniline or BABA and a component selected from epichlorohydrin, ethylenedichloride, and diaminocyclohexane and a third component, formaldehyde. Thus, the polymers useful in water treatment have an aniline requirement which may also include a substituted aniline as an alternate or second component.

Claims

1. A method of reducing turbidity in water which comprises adding to the water a cationic copolymer of copolymerisable compounds comprising (1) 2,4-bis(p-aminobenzyl)aniline (BABA) or aniline and (2) at least one of (a) epichlorohydrin, (b) ethylene dichloride and (c) formaldehyde.
2. A method according to claim 1 wherein one of the copolymerisable compounds is epichlorohydrin.
3. A method according to claim 1 or 2 wherein one of the copolymerisable compounds is ethylene dichloride.
4. A method according to claim 1, 2 or 3 wherein one of the copolymerisable compounds is formaldehyde.
5. A method according to any preceding claim wherein (1) is BABA and the molar ratio of (1) to (2) is from 1:1 to 1:4.
6. A method according to claim 1 or 5 wherein said cationic copolymer is a cationic terpolymer of (1), formaldehyde, and epichlorohydrin or ethylenedichloride.
7. A method according to claim 1 or 5 wherein said cationic copolymer is a cationic terpolymer of (1), tetraethylene pentamine, and formaldehyde.
8. A method according to claim 1 or 5 wherein said cationic copolymer is a cationic terpolymer of (1), ethylene dichloride/ammonia, and formaldehyde.
9. A method according to any of claims 1 to 6 and 8 wherein the cationic copolymer is a copolymer of (1), (2), and a further compound copolymerisable therewith.
10. A method according to claim 9 wherein the further compound is selected from diaminocyclohexane, tetraethylene pentamine, hexamethylenediamine, diethanolamine, hexamethyleneimine, polyamines, C_{12} — C_{18} fatty amines, and phenols.
11. The use, in reducing the turbidity of turbid water, of cationic copolymer of copolymerisable compounds comprising (1) BABA or aniline and (2) at least one of (a) epichlorohydrin, (b) ethylene dichloride and (c) formaldehyde.
12. A method of reducing water turbidity by use of a cationic copolymer, the method being substantially as hereinbefore described in any Example.
13. A water turbidity reducing cationic copolymer as defined in any of claims 1 to 10.
14. A BABA copolymer according to claim 12.
15. A copolymer according to claim 13 or 14 substantially as hereinbefore described in any Table or Example.